

AMENDMENTS TO THE SPECIFICATION

IN THE SPECIFICATION:

The paragraph on page 1, line 2, please make the following changes:

The present invention concerns a method ~~in~~ for the fabrication of an organic thin-film semiconducting device, wherein the semiconducting device comprises an electrode arrangement with electrodes contacting the semiconducting organic material.

The paragraph on page 1, line 11, please make the following changes:

A paper by M.Granström & et al. "Laminated fabrication of polymeric photovoltaic diodes", Nature, Vol. 395, pp. 257-260, discloses a photovoltaic diode with a double layer of semiconducting polymers. Photoexcited electron transfer between donor and acceptor molecular semiconductors provides a method of efficient charge generation after photoabsorption and can be exploited in photovoltaic diodes. But efficient charge separation and transport to the collector electrodes are problematic, because the absorbed photons must be close to the donor-acceptor heterojunction, while at the same time good connectivity of the donor and acceptor materials in the respective electrodes is

required. Mixtures of acceptor and donor semiconducting polymers can provide phase-separated structures, which to some extent meet this requirement, ~~providing~~ and provide high photoconductive efficiencies. To this end Granström & et al. disclose two-layer polymer diodes where the acceptor material is a fluorescent cyano derivative of poly (*p*-phenylene vinylene) (MEH-CN-PPV) doped with a small amount of a derivative of polythiophene (POPT). The acceptor layer is contacted by an electrode and covered by a glass substrate. The acceptor layer is laminated together with a donor layer of POPT doped with a small amount of MEH-CN-PPV which is spin-coated on either indium tin oxide (ITO) substrates or glass coated with polyethylene dioxi~~de~~ thiophene (doped with polystyrene sulphonic acid) (PEDOT-PSS). To ensure a low contact resistance, a thin layer of gold was thermally evaporated on the glass substrate before the PEDOT material was spin-coated thereon. Since Granström & et al. describe a photovoltaic diode, it is evident that they are not concerned with obtaining a high rectification ratio, as is desirable with ~~such as will be desirable in~~ switching diodes, nor is a difference in the work function values of the cathode and the anode an issue, although the materials envisaged for the anode, (ITO, PEDOT and gold) all have a high work function value, ranging from ~~4,8~~ 4.8 for ITO to well above 5 eV for PEDOT and gold, with

the work function values of the latter two being almost ~~similar~~ the same.

The paragraph on page 2, line 6, please make the following changes:

However, it has been found that particularly noble metals such as gold and platinum ~~cause~~ result in a poor quality of a conducting polymer thin film deposited ~~thereupon~~ and very often the polymer film ~~presents~~ has pin holes which are not acceptable when the films are arranged in a sandwiched geometry. Moreover gold is a costly material, ~~but apparently~~ although Granström & et al. ~~have~~ selected gold because of its high work function value matching that of PEDOT-PSS.

The paragraph on page 2, line 12, please make the following changes: ✓

In switching semiconductor devices with diode structures a high rectification ratio at of the latter ~~will be~~ is desirable, ~~and~~ It is also desired that the contact surface between an electrode and a semiconducting polymer ~~should provide~~ provides efficient charge injection, but this latter feature is not of concern for collector electrodes, that are the anodes, in a photovoltaic device based on organic semiconducting materials.

The paragraph on page 2, line 18, please make the following changes:

It is known that the contact surface between a conducting and a semiconducting polymer has superior properties with respect to injection of charge. For example a conducting polymer based on poly (3,4-ethylenedioxythiophene) (PEDOT) possesses a very high work function which makes it suitable as anode in semiconductor components based on organic semiconductors, but the high resistivity of PEDOT limits the performance of components because of a very high series resistance. This is particularly unfortunate when the electrodes are patterned with line widths of the order of 1  $\mu\text{m}$ . However, it is believed that such components shall be crucial to realizing high density memory cells for use in memory modules based on ~~polymer~~ polymers as the memory material, provided that it ~~will be~~ is possible to achieve the desired high data read-out speed. This shall, however ~~depende~~ depend on the ~~possibility~~ availability of highly conducting electrodes for the memory cells which can be manufactured with microfabrication methods.

The paragraph on page 2, line 32, please make the following changes:

The object of the present invention is therefore to provide a method for the manufacturing of an electrode for use in organic semiconductor ~~component~~ components, and such that the electrode combines superior charge injection properties with a high conductivity. Furthermore it is an object of the invention to provide a method which permits the manufacturing of an electrode of this kind with patterned line widths in the order of 1µm. Finally it is also an object of the present invention to provide a method for manufacturing of electrodes which can be used in organic thin-film diodes, with high rectification ratio, or in electrode arrangements in organic thin-film transistors.

The paragraph on page 4, line 1, please make the following changes:

It is according to the method of the invention advantageous ~~selecting~~ to select the conducting polymer in the second layer ~~on~~ as a doped conjugated polymer and ~~then~~ preferably ~~selecting~~ select the conjugated polymer from among poly(3,4-dioxyethylene thiophene) (PEDOT), a copolymer which includes the monomer, 3,4-dioxyethylene thiophene, substituted poly(thiophenes), substituted poly(pyrroles), substituted poly(anilines) or copolymers thereof-, whereas the dopant for the conjugated polymer preferably is poly(4-styrene sulphonate) (PSS).

The paragraph on page 4, line 9, please make the following changes:

In a preferred embodiment of the method according to the invention the doped conjugated polymer ~~as~~ is poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(4-styrene sulphonate) (PSS).

The paragraph on page 4, line 12, please make the following changes:

It is according to the invention advantageous ~~selecting to~~ select the semiconducting organic material in the third layer from among conjugated polymers, or crystalline, polycrystalline, microcrystalline and amorphous organic compounds, and in case the conjugated polymer is selected, it is preferred that this is selected from among ~~the conjugated polymer in the third layer among~~ poly(2-methoxy, 5-(2'-ethylhexyloxi ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) or poly(3-hexylthiophene) (P3HT).

The paragraph on page 4, line 19, please make the following changes:

Finally it is according to the invention advantageous ~~selecting to~~ select the metal of the fourth layer from among metals which have a lower work function than that of the anode and ~~then~~ to

particularly ~~selecting~~ select the metal of the fourth layer as the same as the metal selected for the first layer, but aluminium could in any case particularly be selected as the metal of the fourth layer.

The paragraph on page 4, line 28, please make the following changes:

The invention shall now be described in more detail with reference to the accompanying ~~drawing~~ drawings as well as an appended example of polymer-based diodes with high rectification ratio manufactured according to the method described in the present invention.

The paragraph on page 6, line 7, please make the following changes:

The present invention can be used to realize electrode arrangements for organic semiconductor components in thin-film electronics. In the anode a conducting polymer is used in the form of a conjugated polymer to which has been added a suitable dopant. Fig.1 shows a structure of such a conducting polymer where the conjugated polymer is poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(4-styrenesulphonate) (PSS). This type of conducting polymer shall ~~in the following~~ be termed as PEDOT-PSS. Fig 1b shows

the structure of a semiconducting conjugated polymer belonging to the class of polythiophenes, namely poly(3-hexylthiophene) (P3HT) and fig. 1c shows the structure of another semiconducting conjugated polymer, belonging to the class of polyphenylenevinylenes, namely poly(2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV). The use of these materials is well-known within organic semiconductor technology.

The paragraph on page 6, line 21, please make the following changes:

Fig. 2a shows a first embodiment of a diode in thin-film electronics made by the method according to the present invention. On a substrate 1 which is made ~~by~~ from an electrically insulating material, e.g. glass or silicon where the surface is selectively ~~oxidised~~ oxidized to ~~from~~ form silicon dioxide, there is patterned an electronic conductor with good conductivity, for example a metal in the form of thin stripes 2 which constitute a first layer 2 in the diode. The metal may be chosen among calcium, manganese, ~~aluminium~~ aluminum, nickel, copper or silver. Since the layer 2 constitutes a part of the anode in the diode, it might seem reasonable to select a metal with high work function value, for example Au or Pt as known in the prior art. However, these noble



metals are more or less chemically inactive and at least as far as gold is concerned, also have a tendency to migrate into adjacent layers. Also gold should be avoided for reasons set out in the introduction. Therefore, according to the invention a metal with low work function shall be selected, for example copper, ~~aluminium~~ aluminum or silver which provide good adhesion to the overlying second layer 3 which is made with a conducting polymer with high work function values. According to a preferred embodiment of the invention the second layer 3 employs a conducting polymer in the form of PEDOT doped with PSS. In fig. 2a this second layer 3 of PEDOT-PSS, is patterned conformally with the first layer 2, and the combination metal/PEDOT-PSS now constitutes the anode 2,3 of the diode. Above the anode 2,3 there is now provided a third layer 4 of a semiconducting polymer. According to a preferred embodiment of the invention the third layer is made of a semiconducting polymer, for instance preferably poly(2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV). Other semiconducting polymers may also be used, e.g. poly(3-hexylthiophene) (P3HT) ~~may be relevant~~. Over the third layer 4 of semiconducting material the cathode 5 is now applied as a stripe electrode made from a metal with a suitably low work function value. This metal may e.g. be ~~aluminium~~ aluminum, but is not limited thereto and may in principle be made from other

materials with comparable electronic properties, e.g. indium tin oxide (ITO). The diode in fig. 2a now appears as a sandwich structure with the anode made from several patterned stripe electrodes and shall be representative for embodiments where the active area, i.e. the semiconductor layer 4 typically is of the size in the order of 1-100  $\mu\text{m}^2$ .

The paragraph on page 9, line 28, please make the following changes:

According to the present invention anodes formed as double layers with metal, or alternatively a semiconductor or a semiconductor and a metal in combination, under a layer of a conducting polymer in the form of PEDOT-PSS ~~shall improve~~ improves the conductivity. The metal and the semiconductor in the anode may be Cu or Al which both possess a low work function, but in combination with PEDOT the anode appears with essentially the high work function of PEDOT. At the same time the combination of metal and PEDOT improves the conductivity of the anode. The PEDOT-PSS layer modifies the injection properties of the anode metal which has a low work function value, providing a problem-free hole injection. If the anode were made from metal only, the current flow would be limited by the contact, but the use of PEDOT-PSS ensures

that the current flow now ~~shall~~ is be bulk-limited. ~~By~~ By using a metal/PEDOT-PSS-anode it is, as shown in fig. 3f, possible to make diodes with a rectification ratio of up to seven orders of magnitude. A major advantage which is achieved by employing an anode of metal and a conducting polymer, is the possibility of being able to pattern the anode. The use of metal under PEDOT yields higher conductivity along the electrodes compared to the conducting polymer itself. Even with patterned electrodes with line widths of the order of  $1\mu\text{m}$ , high current density can be achieved in combination with superior charge injection properties. This can be used to realize memory cells in polymer memories with high data storage density and it becomes possible to achieve high read-out speeds because of the highly conducting electrodes. At the same time the memory cells may be realized with line widths in the order of  $1\mu\text{m}$  by suitable patterning of the metal/polymer layer. In this connection it should be remarked that the contact between any metal in the anode and a highly doped conducting polymer shall be ohmic.

The paragraph on page 10, line 24, please make the following changes:

A large effort has been undertaken towards fabrication of electronic devices using polymers. Most of these are directed

towards field effect transistors and diodes, in imitation of silicon electronics. Among the diodes, both light emitting diodes and light detecting diodes constitute the major fraction of the studies; in both of these a transparent electrode is suitable. However, a high rectification organic diode is quite important for a broad spectrum of electronic applications. In order to fabricate diodes based on semiconducting polymers with high rectification, one needs materials that allow efficient charge injection through the polymer under forward bias, and much less so under reverse bias. Normally this is achieved using materials that match in energy position, or make low potential barriers, to the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels of the polymer. In the reverse bias both barriers for electrons and holes must be high enough to keep the current low, having thus as a result a high rectification ratio. But it is not just the energy levels that matter. The interface properties and the quality of the polymer film formed onto a given metal can define the diode properties; often polymer film spin-coated onto inert materials such as gold presents pin holes that is are not acceptable, if one needs to evaporate an upper electrode on top of the polymer film, in a sandwich geometry. The conducting/semiconducting polymer interface tends to have good

adhesion. The oxidized conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulphonate) (PEDOT-PSS) was found to have the high work function value ~~5.2~~ 5.2 eV which allows efficient hole injection in LEDs or collectors in photodiodes. However, the higher resistance of PEDOT-PSS compared with ordinary metals may compromise the diode performance in thin patterned lines, due to voltage drop under high currents. To handle this problem, a metal layer under the polymer is used. Any metal can be used as the underlying layer as it is not necessary to match the work function of the metal ( $\Phi_m$ ) with the work function of PEDOT ( $\Phi_{\text{PEDOT}}$ ). Diodes made with several metals (Al (~~4.2~~ 4.2 eV), Ag (~~4.3~~ 4.3 eV), Cu (~~4.5~~ 4.5 eV)) were tested. In all cases the current flow of holes which was contact-limited, changed to bulk-limited when a PEDOT-PSS layer was used between the anode metal and the semiconducting polymer MEH-PPV (poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene)). In order to study the electrical properties of diodes with different active areas copper was chosen as the underlying layer, particularly due to its good stability and etching properties. The Cu/PEDOT-PSS interface was demonstrated to be ohmic with a contact resistance  $r_c \approx 7 \Omega/\square$ . The ohmic behaviour of Cu/PEDOT-PSS interface is an important asset for its use as an electrode in diodes. The contact resistance of

Cu/PEDOT-PSS interface was measured using planar geometry to provide a copper surface similar to that used for the diodes.

The paragraph on page 13, line 23, please make the following changes:

The Cu/PEDOT-PSS/MEH-PPV/Al diodes with  $100\text{ }\mu\text{m}^2$  of active area presented a similar shape of the forward current-voltage characteristics, as can be seen in the insert graph in fig 5. In order to compare the I-V characteristics of both diodes, the current ~~density~~ densities are plotted in fig. 5 both for the diode ~~in of~~ fig. 4 ( $8\text{mm}^2$ ) and for the diode with  $100\text{ }\mu\text{m}^2$ . The shift in the absolute value of the current can be ~~understood due~~ correlated to the thickness difference between the diodes. The scaling is quite consistent.

The paragraph on page 14, line 1, please make the following changes:

However, for a diode of this size the current level is quite low, around the noise level as can be seen in the insert graph in fig. 5. The I-V characteristics for the current ~~density~~ densities of both the diode with  $1\text{ }\mu\text{m}^2$  active area and the one of  $8\text{ mm}^2$  active area are plotted. The function  $J(V)$  for the smaller diode is

plotted up to twenty volts. It ~~will~~ can be seen that ~~its~~ the behaviour and shape do not scale very well with the larger diode. ~~In~~ With these small diodes, the area extension is only ten times the thickness of the layers, and fringe fields are expected to start becoming important; even more important may be the existing irregularities causing any geometrical estimates to err.

The paragraph on page 14, line 10, please make the following changes:

The electrical transport properties of conjugated polymers and polymer/metals junctions ~~has~~ have been studied for quite some time. The first attempt in modelling the PPV-based diodes ~~were~~ was based on the Fowler-Nordheim model describing the tunnelling process in the diode. It was possible to obtain the approximate values for barrier heights and for the polymer energy levels. A number of models ~~has~~ have since then been presented, taking in account more parameters for detailing the interface properties. It is proposed that when the current is contact-limited ~~it~~ the effect of Coulomb trapping of carriers at the interface can be determined by the image force, ~~the effect of Coulomb trapping of carriers at the interface~~. This trapping results in an increase of the energy barrier height, decreasing the injection flow. It was concluded

that the presence of an insulating material free of traps could increase the charge injection. In the case of PEDOT-PSS it was shown that during the deposition of this material by spin-coating, a segregation of PEDOT and PSS takes place. PSS is an insulating material and it was found to form a thin layer all over the PEDOT surface film. This thin layer cannot trap charges from the electrode which may account for the improvement in the carrier injection from PEDOT. The bulk-limited current of MEH-PPV has been studied and reported by several research groups. It was found that at high fields MEH-PPV presents a spatial charge limitation of the current, and also that mobility is dependent on the applied electric field. In the present case the behaviour is similar, as the current does not depend on  $V^2$  precisely because of the field-dependent mobility. This was proposed in a recent study by Malliaras & et al., PRB, Vol 58, R13411 (1998). The use of a model developed by P. N. Murgatroyd (J. Phys. D. Vol. 3,151 (1970)) combines spatial charge limitation dependence with the non-constant mobility in the same equation. From these models one can evaluate the data obtained herein by plotting the high field current in the function format  $JL^3$  versus  $(VL)$ , where  $J$  is the current density,  $L$  the polymer thickness and  $V$  the applied voltage minus the built-in voltage of the diodes. For the present invention this enabled a



data fit and gave similar values for the polymer parameters,  $\mu_0$  and  $E_0$ , i.e. the zero field mobility and the characteristic field respectively.